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14. ABSTRACT This research was directed towards the development of fundamental understanding of the connections amongst the microstructure, processing and macroscopic properties of polymeric based nanocomposites. Blending of 0-, 1-, and 2-dimensional inorganic fillers such as POSS, carbon nanotubes, and nano-clay platelets into polymeric matrices enabled exploration of various filler/matrix combinations on mechanical properties.						
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Defense University Research Initiative on Nanotechnology:

**Microstructure, Processing and Mechanical Performance
of
Polymeric Nanocomposites**

Final Report

June 15, 2001 – August 31, 2006

Principal Investigators: Mary C. Boyce,
Gail E. Kendall Professor of Mechanical Engineering

Edwin L. Thomas,
Morris Cohen Professor of Materials Science and
Engineering

Institute: Massachusetts Institute of Technology
Department of Mechanical Engineering
Room 1-304
77 Massachusetts Avenue
Cambridge, MA 02139

Agreement Number: F49620-01-1-0447

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1.Team Members

Faculty:

Mary C. Boyce (PI), Gail E. Kendall Professor of Mechanical Engineering, MIT
Edwin L. Thomas (co-PI), Morris Cohen Professor of Materials Science & Engineering, MIT
Robert E. Cohen, St. Laurent Professor of Chemical Engineering, MIT
Karen G. Gleason, Professor of Chemical Engineering, MIT
David M. Parks, Professor of Mechanical Engineering, MIT
Gareth H. McKinley, Professor of Mechanical Engineering, MIT
Gregory Rutledge, Professor of Chemical Engineering, MIT
William Brittain, Professor of Polymer Science, University of Akron

PostDoctoral Associates:

Jeff Abes, Chemical Engineering, MIT (Summer 2003 - no salary from Durint)
Jose Bico, Mechanical Engineering, MIT (July 2003)
Thomas Breiner, Materials Science, MIT (Feb 02 – Apr 03; half-time)
Franco Capaldi, Mechanical Engineering, MIT (Feb 2005-June 2005)
Sabine Cantournet, Mechanical Engineering, MIT (September 2004-August 2005, partial support DURINT, partial support ExxonMobil)
Christian Honeker, Materials Science, MIT (June 2001 – Sept, 2001)
Jijun Huang, Mechanical Engineering, MIT (Jan 2006 – May 2006; half-time)
Amrit Kalra, Chemical Engineering, MIT (Sept 1 2003 – July 2004)
Vikram Kuppa, Chemical Engineering, MIT (July 2004 – July 2006, half-time)
Younghwan Kwon, Chemical Engineering, MIT (June 1, 2001- Aug 2002)
Hojun Lee, Mechanical Engineering, MIT (Jun 01 - May 30, 2003)
Young Jun Lee, Mechanical Engineering, MIT (June 1, 2003 – May 30, 2004)
Leslie Loo, Chemical Engineering, MIT (Sept 01– July 03)
Oleg Manevitch, Chemical Engineering, MIT (Jan 02 – June 02)
Pieter In't Veld, Chemical Engineering, MIT (no salary from Durint)
Yijin Xu, University of Akron (9/15/01-present)
Bin Chen, Mechanical Engineering (8/15/03-9/04; funded by Teijin, Inc)

CMI PostDoctoral Associates:

Russell Gorga, Chemical Engineering
Kenneth Lau, Chemical Engineering
Antonio Pantano, Mechanical Engineering
Ytzik Tsabba, Materials Science and Engineering

Graduate Students:

Christian Grippo, S.M. Mechanical Engineering December 2003.
Edwin Chan, S.M., Materials Science and Engineering, MIT August 2003.
Theodoros Akiskalos, Mechanical Engineering, MIT, May 2004.

Mohit Garg Mechanical Engineering , MIT (September 2003- July 2006 (Durint support 2005-2006)

Roger Aronow, Chemical Engineering, MIT (Jan. 2003 – May 2006)

Ethan Parsons, Mechanical Engineering, MIT (Sept. 2002 – Jan 2003)

Nuo Sheng, Mechanical Engineering, MIT (June 2001 – June 2006)

Theodora Tzianetopolou, Mechanical Engineering, MIT (Nov 2001 – Jan 2003)

Franco Capaldi, Mechanical Engineering, MIT (Sept 2001 – Feb 2005)

Mats Danielsson, Ph.D. August 2003, Mechanical Engineering, MIT (Sept 2002 –Jan 2003)

Alberta Gallino (visiting student from U. Milano) (Aug 2001 – Feb 2003)

Yung-Hoon Ha, Ph.D. Materials Science and Engineering May 2003,

Panitarn Wanakamol, Materials Science and Engineering, MIT (July 2001 –July 2007)

Edward Kopesky, Chemical Engineering, MIT (Jan 2002 –June 2005)

Yonathan Thio, Ph.D. Chemical Engineering, MIT May 2003 ; partial DURINT support

Michelle Poliskie, Chemical Engineering, MIT (Sept 2002 – Aug 2005)

Adam Mulliken, Mechanical Engineering, MIT (DURINT support, June 2005-June 2006)

Sharon Soong, Chemical Engineering, MIT (DURINT support, Sept 2004-Sept 2005)

Bernadette Higgins, University of Akron

Sang Hoon Lee, University of Akron

Carlos Aquilar-Solis, University of Akron

Domitille Pitart, visiting student, CNRS, France (June – Aug, 2006).

External Collaborators:

John Gilmer, Eastman Chemical Company

Andy Tsou, ExxonMobil

Alan Windle, Cambridge University

John Robertson, Cambridge University

William Milne, Cambridge University

Tim Haddad, Edwards Air Force Research Lab

Rusty Blanski, Edwards Air Force Research Lab

Alex Hsieh, Army Research Lab

Donald Rivin, Natick Army Research Lab

Jo Ann Ratto, Natick Army Research Lab

Seng Tan, WPAFB

Tai Benson-Tolle, WPAFB

Richard Vaia, WPAFB

David Carnahan, Nanolabs

Z. Ren, Boston College

2. Research Program Objectives

This research was directed towards the development of fundamental understanding of the connections amongst the microstructure, processing and macroscopic properties of polymeric based nanocomposites. Blending of 0-, 1-, and 2-dimensional inorganic fillers such as POSS, carbon nanotubes, and nano-clay platelets into polymeric matrices enabled exploration of various filler/matrix combinations on mechanical properties. The principal goals of the proposed research program were:

- Development of a fundamental understanding of the connections among microstructure, processing, and macroscopic properties of polymeric nanocomposites having 0D, 1D and 2D reinforcing particles
- Development of in situ synthesis and blend processing to realize optimum microstructures of nanocomposites
- Development and application of novel experimentation and observation tools for assessing structure and properties of polymer nanocomposites
- Development of models and modeling tools from molecular to mesoscopic to macroscopic for predicting polymeric nanocomposite behavior and, ultimately, designing polymeric nanocomposite microstructures for specific target properties

These goals were met through a collaborative, interdisciplinary five-year research program involving faculty in a range of disciplines from synthesis to rheology to processing to microscopy to spectroscopy to mechanical evaluation to molecular modeling to micromechanical modeling to continuum level modeling. Key to our approach was the requisite expertise in all aspects from basic synthesis of important model systems, to processing into specimens for microstructural and mechanical characterization. In addition, our industrial partners provided commercial samples processed using standard equipment. Modelling efforts spanned the continuum to the molecular, developing a hierarchical framework for multiscale simulations of mechanical behavior and other properties of the nanocomposites. The principal property under investigation was mechanical behavior. However, nanocomposites offer many other opportunities and effort was also dedicated to examining electrical conductivity, permeability and temperature use range so as to explore and optimize the truly multifunctional property potential of polymer nanocomposites.

3. Research Accomplishments

This research program on Microstructure, Processing and Mechanical Performance of Polymeric Nanocomposites began on June 15, 2001. This final report covers the period of June 15, 2001 through August 31, 2006. The research program was executed in a collaborative manner by eight faculty together with their graduate students and postdoctoral associates as well as close interactions and collaborations with key industrial and government research scientists and engineers. Research efforts focused on the synthesis, processing, microstructural and morphological characterization, mechanical evaluation, and modeling of selected polymeric nanocomposite materials. The materials under this study included nano-clay/thermoplastic composites, nano-clay/thermoset composites, nano-clay/blockcopolymer nanocomposites, POSS-enhanced polymeric nanocomposites, nano-particulate/thermoplastic nanocomposites and carbon nanotube/polymer nanocomposites. Unifying issues that we have found to be common to all systems are first discussed followed by specific details on research progress for each of the 0D, 1D, and 2D nanoparticle/polymer nanocomposites systems. The interactions and collaborations amongst the faculty and groups are demonstrated within the research descriptions below.

Several key unifying issues/themes for determining, understanding and optimizing properties for all classes of polymer nanocomposites were identified through this research program. A key feature of primary importance in understanding the nanocomposite is the actual identification and definition of the structure and the properties of the nanoparticle itself; whether the nanoparticle be 0D, 1D or 2D, it is critical to provide a well defined description of the particle geometry, structure and properties and its surrounding zone of influence on the matrix morphology and properties and its interface with the matrix in order to assess the impact of the nanoparticle on the nanocomposite property. Towards that end, we identified a clear route for obtaining mechanical properties of nanoparticles such that the properties are consistent with a continuum level property definition via use and interpretation of molecular level simulation results. We utilized this approach to describe the effective mechanical behavior of carbon nanotubes and nanoclay particles. Similar developments addressed POSS "particles" which are observed to have very different mechanical properties if acting as isolated entities or as crystallized (or near crystallized) rafts – a basic, but somewhat different, observation also seen in nanoclay particles when comparing intercalated particle structure/properties with that of the exfoliated condition. Furthermore, POSS particles were found to have the ability to act as either stiffening agents or as plasticizing agents depending upon the interactions between the functional groups and the matrix polymer. Another key issue was the development of synthesis and processing routes to (1) properly disperse the particles within the matrix in order to fully make use of their nanoscopic potential and (2) to provide a good bonding with the matrix in order to facilitate load transfer from the matrix to the particle in order to exploit the stiffening and strengthening potential of the nanoparticle, the degree of such load transfer can be identified through proper use of in situ spectroscopy data. A third key issue is proper identification of the effect of the nanoparticle on the surrounding matrix where use

of microscopy, spectroscopy and molecular and continuum level simulation prove enlightening on identifying the effects on the structure and the local dynamics of the polymer molecules. Additionally, the importance of particle orientation and accurately identifying the degree of particle orientation is a major factor in mechanical and transport properties; such orientation descriptions can be found through microscopy and imaging processing, but here we also found the use of infrared spectroscopy as a technique for obtaining the orientation distribution of particles. Details specific to these key issues and others for each material system are presented below where we note that each effect manifests itself differently in each of the nanocomposite material systems.

3.1 0D Nanoparticle/Polymer Nanocomposites

Composites reinforced with particles that are nanoscopic in all dimensions (i.e. “0D nanoparticles”) have been characterized rheologically, morphologically, spectroscopically and by computer simulation. The specific systems under study include conventional inorganic filler like calcium carbonate (CaCO_3) and polyhedral oligomeric silsesquioxane (POSS) particles of particular interest to Air Force researchers (Tim Haddad et al) at Edwards Air Force Base. Furthermore, POSS is now known (see below) to exhibit strong tendency to crystallize into 2D “rafts” when tethered to the polymer chain, permitting a unique opportunity to investigate the role of filler dimensionality using a common chemistry.

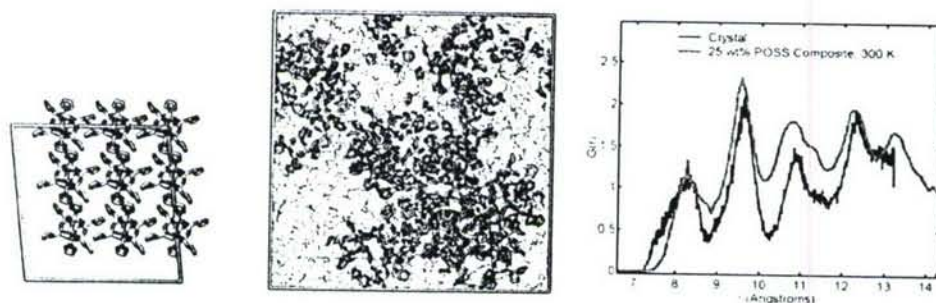


Figure 1. Molecular simulation of a POSS crystal; POSS aggregating within a polymer matrix forming a crystal; and the radial distribution function for the pure POSS crystal compared to the POSS aggregate within the polymer predicting the tendency of POSS to form raft-like structures within polymer nanocomposites [Capaldi, Rutledge, and Boyce (2003)].

Rheological investigations were performed by **Kopesky, Cohen and McKinley**, in collaboration with **Haddad** of Edwards AFB, on cyclopentyl- and cyclohexyl-modified POSS (cp-POSS, cy-POSS), copolymers containing cp-POSS and cy-POSS tethered to a PMMA backbone (synthesized by **Haddad**), and homopolymer PMMA. Samples were prepared using a twin-screw melt mixer and the resulting blend properties characterized by rheology and dynamical thermal analysis. The degree of dispersion was investigated using WAXD and TEM. Rheological measurements well above T_g have been used to determine the time-temperature superposition behavior of these thermorheologically simple materials. Interestingly, at small volume fractions, free (untethered) POSS nano-dispersed in the melt appears to act as a plasticizer, reducing the

magnitude of selected material properties such as plateau modulus or zero-shear rate viscosity at a given temperature, while simultaneously causing a decrease in free volume (estimated from WLF coefficient analysis). As the volume of dispersed POSS increases, steric effects of the filler dominate and the rheological properties of the melt (modulus, relaxation time, viscosity) are all enhanced. Morphological investigations of the POSS blends and copolymers indicate that there is a significant amount of aggregation (crystallization) of POSS into large particles and raft-like structures. The hydrophobic and oleophobic interfacial properties of fluoro-POSS polymer/nanoparticle blends has been continued in an ongoing collaboration between **Cohen** and **McKinley** with **Haddad** and **Mabry** at Edwards AFB.

To investigate changes in dynamical behavior at the molecular level, proton spin lattice relaxation (T_1) experiments were performed by **Poliskie** and **Gleason** on blends of cis 1,4-polyisoprene and several loadings (1, 5, 10 wt%) of cy-POSS. At 10 wt%, the T_1 time constants of the nanocomposite are indistinguishable from those of the homopolymer. At 1 wt% and 5 wt%, however, the T_1 's and activation energies for molecular motions decrease. It was observed that the compression modulus for the 5 wt% nanocomposite is significantly higher than that of the homopolymer or either of the 1wt% and 10wt% blends. This increase is suggestive of an optimal aggregate size needed to reinforce the matrix.

Modeling of POSS-based nanocomposites at the molecular level has been performed by **Capaldi**, **Boyce** and **Rutledge**. By comparison of experimental and computed crystal structures and vibrational spectra, an appropriate atomistic force field was validated; the vibrational spectra for hydrogen-substituted POSS (h-POSS) were found to have an RMS error of 40 cm^{-1} when compared to experimental data. Molecular dynamics simulation was then performed on the crystal structures of h-POSS and cp-POSS to determine the crystal phase elastic moduli; these moduli were found to vary from 20 GPa for h-POSS to 10 GPa for cp-POSS. Lastly, composites were created by randomly distributing cp-POSS particles (such as those synthesized at Edwards AFB) in a polyethylene matrix. During a 5 ns molecular dynamics simulation, the POSS particles are found to orient with respect to their neighboring particles in a manner reminiscent of the corresponding POSS crystal structures, in accord with experimental observations. The matrix morphology neighboring the POSS was found to engage with the functional groups of the POSS and to be preferentially aligned tangential to the POSS perimeter; this alignment resulted in anisotropy in the local chain dynamics with enhanced polymer dynamics in a direction tangential to the particle and reduced dynamics normal to the particle "interface". Mechanical properties of the nanocomposite were computed by deforming the cell; the POSS was found to increase the stiffness with stiffness increasing with increase in POSS fraction; the stiffness enhancement was also captured using a continuum mechanics based composite analysis following a Mori-Tanaka model by representing the POSS and surroundings as an effective particle with an effective modulus and effective diameter.

Our results, both experimental and modeling, indicated the ability for POSS to very locally interact with the matrix molecules altering their mobility, being able to either

stiffen or plasticize the material. This led us in a direction of exploring the effects of POSS on the rate-dependent mechanical behavior of polymers in studies by **Boyce** and **Cohen** and students **Mulliken** and **Soong**. In the **Mulliken** work, the macroscopic rate-dependent mechanical behavior of polycarbonate compounded with TriSilanolPhenyl-POSS® particles was compared with that of its homopolymer counterpart. On the experimental side, dynamic mechanical analysis tension tests were used to characterize the viscoelastic behavior of these materials, with focus on the rate-dependent shift of material transition temperatures. Uniaxial compression tests on a servohydraulic machine and an aluminum split-Hopkinson pressure bar were used to characterize the rate-dependent yield and postyield behavior. For this particular material system, the POSS has little influence on the polycarbonate glass transition (α) regime. However, the POSS clearly enhanced the mobility of the secondary β motions, significantly reducing the resistance to high rate elastic and plastic deformation. In the **Soong** work, POSS was found to plasticize PVC and hence to dramatically influence its glass transition and corresponding rate-dependent mechanical behavior. Furthermore, with the blending of a small percent of DOP, much larger weight fractions of POSS were able to be blended into the PVC in a completely miscible manner, furthering the range of materials and mechanical properties that can be achieved using POSS as a matrix mobility modifying agent.

To study a possible lengthscale effect of equiaxed particles on mechanical properties, morphological and mechanical studies were performed by **Thio**, **Lazerri** and **Cohen** using CaCO_3 -reinforced isotactic polypropylene. The CaCO_3 particles were of three varieties, with nominal particle sizes of 70 nm, 700 nm and 3500 nm in order to study the particle size scale effect on resulting structure and properties. Debonding and volume evolution in tensile deformation of these composites were performed, with filler volume fractions up to 30%. Axial and lateral dimensions were measured during uniaxial deformation to fracture. Debonding occurred in all samples prior to yield, leading to reductions in the yield and flow stresses as volume fraction increased. Large volume strains were observed beyond yield, and there was an unexpected dependence on the inverse of the particle diameter. This effect could be explained quantitatively by the existence of a 20 nm shell of immobilized polymer surrounding the filler particles. In high speed (IZOD) impact testing, the highest values were seen for the 700nm CaCO_3 particles, a result that could be attributed to better dispersion of these particles using current compounding methods. This study illuminated the competing roles of facilitated debonding and volumetric strain (both favorable in the toughening problem) and the need to scrupulously avoid agglomeration in the nanoparticle filled compounds. Also, the characteristic rate dependent tensile response of the matrix material ligaments between particles is central to the observed level of IZOD impact toughness.

Tailoring tensile behavior (through ternary blending of miscible polymers and plasticizers) to optimize the toughness/stiffness/strength response of 0D nanoparticle-filled nanocomposites was the focus of work by **Aronow** and **Cohen**. An amorphous polymer blend was used to elucidate the effect of matrix properties on toughening mechanisms in polymer nanocomposites comprising equiaxed rigid barium

sulfate filler in a glassy matrix. The ternary blend of two miscible polymers, PMMA and PVC, and plasticizer DOP was used to create sets of material compositions with common values of T_g but significantly different mechanical properties. In general all of the barium sulfate filled composites showed decreasing toughness with increasing filler content. However a few compositions at low loading (ca 5 wt percent) exhibited levels of toughness up to 20 times larger than the unfilled counterpart, with no drop in modulus. SEM examination of these toughened compositions showed that: a) Filler is present both as micron-scale agglomerates as well as dispersed nanoparticles, b) the well-dispersed particles do not debond prior to tensile fracture, c) agglomerates are prone to debonding and internal fracture both of which facilitate desirable (toughness-enhancing) plastic deformation in the matrix. Additionally, micromechanical modeling efforts in the **Parks and Boyce** group by **Parsons** acted to fundamentally explore the effects of particle/matrix bonding on stiffness, strength and toughness through multiaxial, multiparticle micromechanical simulations. Key to validation of the accuracy of these simulation studies was a new video extensometer full field large strain measurement capability developed in this DURINT by **Parsons, Boyce and Parks**.

3.2. *1D Nanoparticles (Carbon Nanotubes)/ Polymer Nanocomposites*

Novel Method for Dispersion of Nanoparticles in a Polymer Matrix: Dispersion of single-wall carbon nanotubes (SWNTs) is critical for many potential applications. **Thomas** and **Tsabba** have developed a novel method for dispersing SWNTs within polymer solutions, based on properties of a dispersed distribution of thin, rod-like colloids, without using strong acid treatments that damage CNTs. Onsager's model of a dilute suspension of such particles shows that the lowest concentration leading to a nematic phase (and hence, to ~gel-like behavior) corresponds to a 0.3wt.% concentration of the SWNTs used, in excellent agreement with the very stable gel-like suspension of SWNTs resulting from the new process. Subsequently, the gel can be treated to disperse the CNTs in a variety of organic solvents; from these, PS/CNT and PMMA/CNT nanocomposites have been made. The distribution of CNTs within the fibers were examined using SEM and image processing by **Boyce, Parks, Akiskalos** and co-workers in **Windle's** group and showed good dispersion. Composite fibers drawn from such nanocomposites by **Cohen** and **Gorga** were tension-tested. However, the stiffness did not increase as would be expected if there was load transfer from the matrix to the CNTs which suggests that there was poor bonding between the CNTs and the matrix.

Solventless Surface Functionalization of Carbon Nanotubes: **Gleason** and **Lau** have functionalized CNTs via chemical vapor deposition to impart targeted surface properties. Conformal coatings of 5-50 nm thickness have been achieved. With **McKinley** and **Bico**, they have shown that PTFE-treated vertically-aligned CNTs (a nanotube 'forest') create a stable superhydrophobic surface, with water contact angles >160 deg. The surface repels water due to both low material surface energy (PTFE) and high surface roughness (forest structure). **Gleason** and **Lau** have also PMMA-treated multi-wall CNTs using plasma CVD. **Cohen** and **Gorga** melt-processed treated MWNTs

with bulk PMMA, and obtained a 50% increase in composite tensile toughness compared with untreated CNTs.

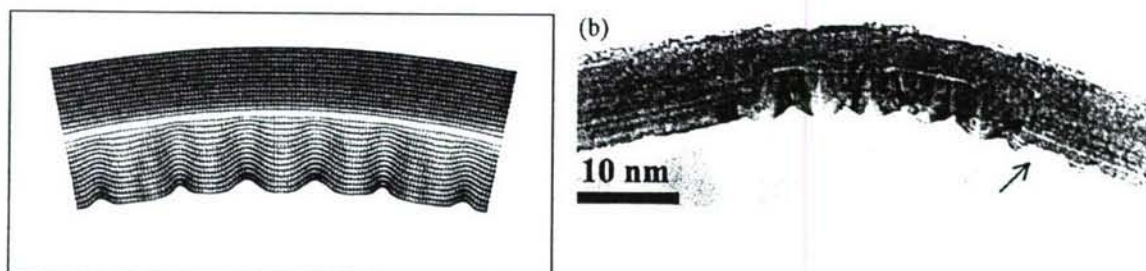


Figure 2 (a) Simulated bending and buckling of a MWNT [Pantano, Boyce and Parks]. (b) High resolution TEM of a buckled MWNT taken from the literature.

Modeling Mechanical Behavior of Single-Wall and Multi-Wall Carbon Nanotubes: **Boyce, Parks, and Pantano** have developed a novel continuum/finite element approach for modeling the structure and deformation of both single and multi-wall CNTs. Individual tubes are modeled using shell elements, where a unique pairing of elastic properties and mechanical thickness of the atomic-thickness tube wall enables successful modeling. Curvature-induced internal stress within the CNT wall is accounted for, as are attractive/repulsive van der Waals forces, crucial in MWNTs and in tube/tube or tube/matrix interactions. The overall modeling approach has been verified by comparing SWNT simulations with MD results in the literature. Further developments of **Parks, Boyce and Pantano** found that atomic-level resolution of carbon atom positions within CNTs of arbitrary chirality can be recovered from finite element models – this enabled direct interaction of mechanical and electrical property calculation where finite element calculations of deformed CNTs were interfaced with tight binding calculations of electrical conductivity in a collaboration with **Nardelli**.

The successful treatment of MWNT mechanics evident in Figure 2 has enabled **Boyce, Parks, and Akiskalos** to begin detailed study of load-transfer mechanics in idealized MWNT/polymer nanocomposites, including matrix/CNT load-transfer and among interior nanotubes. **Akiskalos, Boyce and Parks** also developed statistical meso-mechanical models of aligned CNTs distributed in a polymer matrix, along with parametric treatments of CNT aspect ratio, concentration, and matrix/surface interaction to explore effects on nanocomposite stiffness and strength.

We also note that our success in using a consistent definition of effective modulus and thickness, based on the stretching and bending stiffnesses of the graphene lamella obtained in molecular dynamics simulations, was adopted by **Rutledge and Manevitch** in extraction of these properties for individual (exfoliated) montmorillonite platelets from atomistic simulations. In turn, **Boyce, Parks, and Sheng** have used **Rutledge's** MMT properties in a hierarchical, multi-scale continuum modeling of polymer/clay nanocomposites; similar treatments apply to models of exfoliated clay particles within block co-polymer layers, by **Boyce and Tzianetopoulou**. **Boyce and Qi** used tube-bending rigidities based on the effective wall thickness and modulus and tube

radii and radial spacing and found excellent agreement between their models and nanoindentation experiments on a vertically-aligned multi-wall CNT forest, where the nanoindentation tests were utilized as a method to experimentally obtain the mechanical properties of CNTs using a newly developed model for the nanoindentation of vertically aligned nanofibers.

The development of effective continuum level models of MWNTs was taken one step further in work by **Boyce, Garg and Pantano**, where an equivalent orthotropic representation (EOR) of the nonlinear elastic behavior of multi-walled carbon nanotubes (MWCNTs) was developed based on a nested shell structural representation of MWCNTs of **Pantano, Parks and Boyce**. The EOR model was used together with the finite element method to simulate the large deformation of MWCNTs under bending, axial compression and radial compression. Results were compared with those of the nested shell model for 4-, 8-, 9-, 14-, and 19-walled carbon nanotubes. The EOR model provides a dramatic improvement in computational efficiency and successfully quantitatively replicates the overall deformation behavior including the initial linear elastic behavior, the onset of local buckling, and the post-buckling compliance. The proposed EOR model together with the FE method offers a computationally efficient method for simulating large and complex systems of MWCNTs.

Additionally, the effect of carbon nanotubes on the mechanical behavior of elastomeric materials was investigated by **Cantournet and Boyce** together with industrial partner **Tsou**. The large deformation uniaxial tension and uniaxial compression stress vs. strain behaviors of a representative elastomer was studied both experimentally and through modeling. The elastomer was reinforced with multi-wall carbon nanotubes (MWNTs) and the influence of weight fraction of MWNTs on the large deformation behavior of the resulting composite was quantified. The initial stiffness and subsequent strain-induced stiffening at large strains were both found to increase with MWNT content. The MWNTs were also found to increase the tensile strength and the tensile stretch at break. A systematic approach for reducing the experimental data to isolate the MWNT contribution to the strain energy of the composite was developed. A constitutive model for the large strain deformation behavior of MWNT elastomer composites was formulated, where the effects of carbon nanotubes were modeled via a constitutive element which tracks the stretching and rotation of a distribution of wavy carbon nanotubes. The MWNT strain energy contribution is due to the bending/unbending of the initial waviness and provides the increase in initial stiffness as well as the retention and further enhancement of the increase in stiffness with large strains. The model was shown to track the stretching and rotation of the CNTs with macroscopic strain as well as predict the dependence of the macroscopic stress-strain behavior on the MWNT content for both uniaxial tension and uniaxial compression. This work demonstrated that the waviness of CNTs can actually act in a beneficial way when CNTs are used to reinforce very compliant elastomers – the wavy CNT still contributes substantially to the initial stiffness while the waviness also enables the composite elastomer to still undergo very large strain without failure in a repeatable, reversible manner.

SAXS of multi-wall carbon nanotube (MWCNT) films: Noting that the production of MWNTs yields MWNTs which span a range in diameter and orientation, **Cohen and Wang** have developed a SAXS technique for studying the morphological properties of MWCNT films. This technique is of a mesoscopic length scale, simultaneously sampling over thousands of individual CNTs while remaining small relative to the macroscopic length scale of the films, making it a useful experimental counterpart to existing electron microscopy techniques. Using a form-factor formalism, it was demonstrated that SAXS can be used to extract quantitative values for the distributions of CNT diameters and orientation of the film. The non-invasive nature of the technique coupled with the appropriate length scale of the SAXS beam has allowed us to observe spatial variation in the morphology of these films and understand their responses to mechanical deformations. Accordingly we were able to develop a further understanding of the growth processes and mechanical behavior of these films, which serve as a new template for CNT-polymer composites.

3.3 2D Nanoclay Particle/Block Copolymer Nanocomposites

Block copolymers phase separate into well-defined morphologies with constituent lengthscales of the order of tens of nanometers and thus offer an additional degree of freedom for selectively controlling the positioning of nanofiller particles. Research has focused on the study of the structure and properties of block copolymers (BCP) and block copolymer nanocomposites (BCPNC). Ha and Thomas successfully processed near single crystalline *intercalated* clay BCP nanocomposites using commercial clay which exhibited modest improvements in mechanical behavior. Temperature dependent studies of the *intercalated* composite show reduced dilation of matrix material during deformation as the glassy block becomes less stiff. In order to disperse single clay sheets into block polymers, a successful synthesis of amino terminated PS was necessary [Kwon, Breiner, Cohen and Thomas]. This allowed production of *exfoliated* clay - BCP nanocomposite with single clay sheets sequestered only in the PS domains [Ha, Thomas, Cohen]. During roll casting, the BCP domains template around the individual clay layers leading to a nanoparticle-induced flipping transition wherein the layer orientation relative to that in the roll cast neat BCP film has changed by 90 degrees. This illustrates that nanoparticles can strongly influence texture development in BCPs. For loading parallel to the layers, a decrease in both the tensile modulus and the yield stress of the CBCP relative to the BCP is experimentally observed despite the reinforcement by the high modulus clay. This behavior is due to the greater layer misorientation created by the presence of the individual clay sheets. The CBCP material also shows an earlier onset and higher rate of strain hardening than the neat BCP. Micromechanical finite element simulations of **Tzianetopoulou and Boyce** are used to predict the stress-strain behavior of CBCP and BCP samples loaded parallel to perfectly aligned and flat layers. The simulations establish that 2% addition of clay provides only a modest improvement in modulus and yield stress for loads applied parallel to the layers. The modeling also shows post yield localization of the deformation into shear bands and the interplay of propagating shear bands and the clay sheets which can lead to the observed earlier onset and increase in the strain hardening rate in the CBCP material.

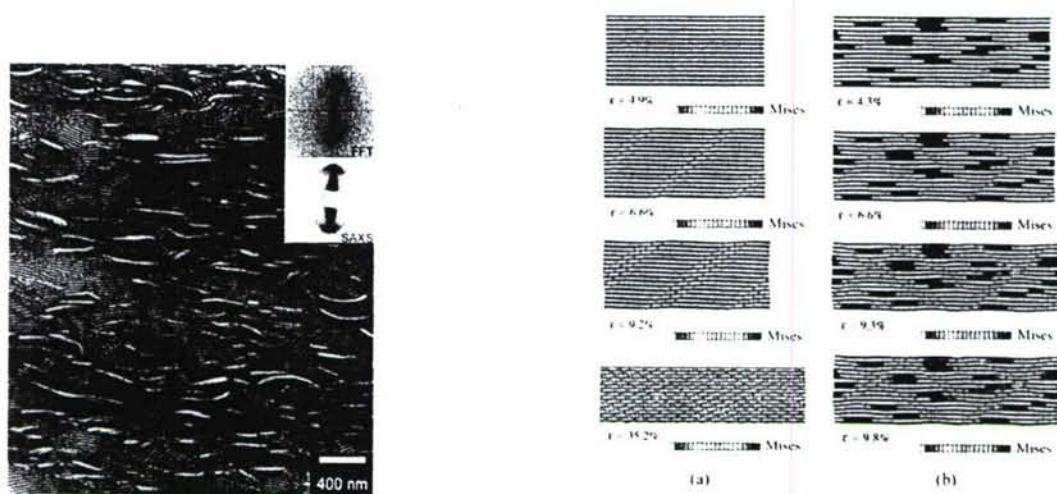


Figure 3. (left) Representative TEM micrograph of lamellar block copolymer containing fully exfoliated nanoclay particles; (right) micromechanical simulations illustrating propagation/cascading of shear bands under tensile loading perpendicular to the lamellar normal for (a) the pure block copolymer and (b) the clay enhanced BCP where the shear band cascading is interrupted by the nanoparticles, thus altering the large strain behavior of these materials.

Intercalated clay-containing near single crystalline lamellar triblock copolymer morphologies were produced via roll-casting. The lamellar microdomains aligned perpendicular to the film surface (the perpendicular orientation), while the clay particles aligned parallel to the film surface (the parallel orientation). Tensile deformation behavior as a function of temperature and deformation direction for the clay-containing system is compared against the neat copolymer system of Cohen et al.¹. The room temperature modulus is 30% higher for films deformed along the lamellar normals (perpendicular deformation) with little difference for films deformed parallel to the lamellae (parallel deformation). No improvements in the tensile modulus of the nanocomposite were observed at higher temperatures relative to that of the neat triblock copolymer. More interestingly, unlike the neat triblock, the presence of the layered-silicates causes necking at room temperature in perpendicular deformation suggesting that the layered-silicates act as nucleation sites for heterogeneous deformation. At temperatures well above the glass transition temperature of the polystyrene, neck formation is however *not* observed suggesting affine deformation previously shown by Cohen et al.¹ for a neat triblock copolymer. Comparison with the affine model developed by Cohen, which states that the macroscopic deformation can be completely traced back to the microscopic tilting and dilation of the lamellar layers, however shows a significant deviation; significantly higher strains are experienced by those lamellar domains most non-parallel to the deformation direction. This illustrates that a heterogeneous deformation is *still* occurring at these elevated temperatures despite no macroscopically observable necking process.

Various groups have studied deformation of multi-granular block copolymers using SAXS and TEM and gained insights on deformation mechanisms. However, real space and real time monitoring is desirable. Moreover, in order to understand the role of

grain boundaries and nanoparticles on the resultant deformation, well designed, controlled microstructure experiments must be pursued. Inducing grain boundaries especially in a controlled manner is a crucial step in understanding how the grain boundaries affect the deformation. **Wanakamol** and **Thomas** created techniques to make materials with isolated and specified grain boundaries which enabled the fundamental study of the effects of grain boundaries on constraining deformation in neighboring grains. In situ deformation experiments of these novel films were conducted using SAXS at CHESS and at Brookhaven as well as at a larger, macroscopic lengthscale using specially gridded samples, imaging the grid during deformation. Several important types of grain boundaries were examined, including 90 tilt ("T") and various twist boundaries.

The single grain, bicrystal and multigrain behaviors were further explored in the micromechanical and constitutive modeling studies of **Tzianetopoulou** and **Boyce**. A general micromechanical framework for the derivation of large strain continuum constitutive models for hyperelastic materials with layered micro- or macro-structures was developed. The framework was implemented for the case of oriented (single-crystal) lamellar BCPs with Neo-Hookean phase behavior, and an analytical continuum model was derived for their large-strain hyperelastic response. The model was used to study the behavior of styrene-butadiene-styrene (SBS) triblock polymers, the behavior and micromechanics of which have been extensively investigated experimentally by the **Thomas** group. Micromechanical unit-cell calculations were used as direct parallels to experimental (x-ray, microscopy, and stress-strain) data in order to verify the model's predictions. The presented continuum model describes the stress and deformation response of an oriented microstructure accurately, and was further implemented in bicrystal and multigranular numerical studies for the mechanical behavior of polycrystalline lamellar configurations. Simulations of the polycrystal structures reveal the manner in which the individual grains collectively deform and interact with each other to accommodate the macroscopic deformation. These results reveal the key roles of interlamellar shearing, lamellar dilation, rotation, and buckling.

3.4. 2D Nanoclay/Thermoplastic and Thermoset Nanocomposites

Nanoclay/polymer nanocomposites have been explored on a variety of fronts as described below.

The **Brittain** group has optimized the "heterocoagulation method" for the synthesis of nanocomposites. This method involves mixing a cationic latex with an aqueous dispersion of unmodified clay. Stable exfoliated nanocomposites require the use of a participating surfactant that created covalently bound cationic groups on the polymer chains; however nanocomposites prepared in this manner are not always processable. A systematic program was initiated to synthesize processable nanocomposites examining the influence of the nature of participating surfactant (initiator, monomer or chain transfer agent), effect of free surfactant, and the mixing method of clay and latex on the end processability of the nanocomposite. This optimized method has now been applied to variety of polymer nanocomposite systems detailed below.

PMMA/clay nanocomposites were studied to understand the influence of clay type (laponite, hectorite and fluorohectorite) and loading on the processing, thermal

stability and morphology. Laponite® and GelWhite® nanocomposites exhibited fully exfoliated structures up to 5% clay while Closite® and Somasif® nanocomposites were exfoliated only at lower clay loadings (generally below 3%). The exfoliated morphology was maintained after melt extrusion or solvent casting. Thermal stability was improved but did not depend on clay dimension (which argues against a theory that thermal stability is related to barrier properties); stability did change with the amount of iron and aluminum present in the clay. Collaboration with **McKinley** has been critical to a better understanding of processing and important variables such as clay dimension.

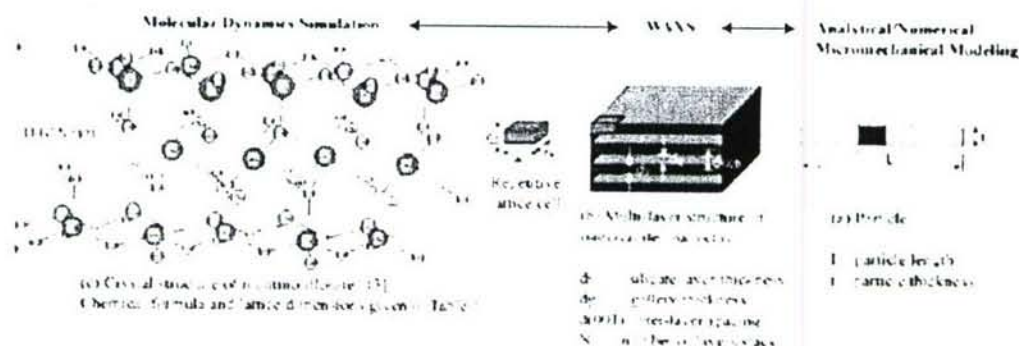
Wang, McKinley and Cohen constructed a fundamental descriptive framework for describing the rate and strain dependent melt rheological properties of several PMMA nanocomposites. Through a combination of high-strain extensional viscosity and small amplitude oscillatory shear measurements, coupled with microstructural morphological characterization we demonstrated that the presence of high aspect ratio clay fillers provide significant viscosity enhancement, the extent of which depends quantitatively on volume fraction, aspect ratio, and deformation rate. For highly extensional flows, this enhancement in the melt rheology disappears at high strains as the platelets become aligned. We also studied the extensional rheology of PMMA-POSS nanocomposites which compared well to previous small strain rheological studies, demonstrating plasticization of PMMA. Above the solubility limit of POSS in PMMA (~ 15% w/w) a large enhancement in viscosity is achieved for low Deborah number flows. In all systems our experimental results corresponded well with previously developed theories for filled systems and percolated networks. These investigations provided insight into the intimate coupling between microstructure and rheology and ultimately into the processability of PMMA nanocomposites.

Elastomer/ montmorillonite (MMT) nanocomposites were prepared using ethyl acrylate and *n*-butyl acrylate. The presence of MMT did not affect the glass transition temperature. Thermal gravimetric analysis indicated that the thermal stability was improved with increasing clay. Exfoliated polystyrene (PS)/MMT nanocomposites were obtained for MMT loadings <4%. The PS/MMT nanocomposites have shown a 70° increase in thermal stability for higher clay loadings. The PS nanocomposites process at lower temperatures than the PMMA system, which reduces the amount of sample discoloration in the extruded samples. Successful molding conditions have been developed for the PS nanocomposites and preliminary mechanical testing data have been generated.

A rheology and microprocessing facility for various polymer/nanofiller samples has been established by the **McKinley** group in the Hatsopoulos Microfluids Laboratory at MIT. This facility enables rapid characterization of small batch samples (in the 5-10 gram range). Polymers that have been compounded to date include PMMA, Nylon, and a Teflon copolymer. Nanofillers that have been studied include a number of different nanoclays (synthetic laponite, as well as numerous grades of cation-exchanged natural montmorillonite clays). A series of rheological studies by **McKinley** and **Lee** in conjunction with **Hsieh** (ARL) using PMMA/clay nanocomposites as well as polystyrene/clay/oligomer ternary blends has enabled the quantitative description of the

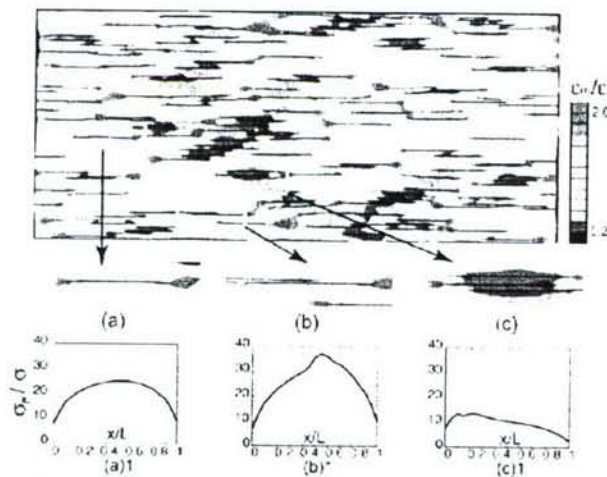
individual contributions of polymer-clay and clay-clay interactions to the total mechanical stress in the fluid. A constitutive model for the linear viscoelastic properties has been developed that represents the individual clay and polymer contributions to the total stress. A series of experiments with increasing clay loadings have shown that the appearance of a yield stress and low frequency plateau modulus at the percolation threshold can be understood *quantitatively* in terms of geometric packing arguments. The time-scale of the percolated system can be understood by considering the rotational diffusivity of the discotic particles.

Beyond the percolation threshold, large amplitude oscillatory shear (LAOS) studies demonstrate the existence of a strongly nonlinear strain-dependence or 'Payne effect' analogous to that observed in carbon-black filled systems. This leads to very long time scale relaxation dynamics and a strong shear-history dependence in sample orientation which has been documented by WAXD, TEM and pole figure analysis.



The connections between the microstructures resulting from the different synthesis and processing routes and the end mechanical and permeability properties have been explored with a range in modeling techniques. A multiscale modeling strategy has been developed to account for the hierarchical morphology of the polymer-clay nanocomposite by **Sheng, Boyce, Parks and Rutledge**. Intercalated nanoclay is represented as a homogeneous "effective particle", whose geometry and mechanical properties depend on underlying structural and constitutive parameters of the nanoclay, such as the number of silicate layers per stack, the inter-layer spacing and the mechanical properties of a single silicate layer obtained from molecular level modeling. This technique has been utilized to study and predict both mechanical (**Sheng, Boyce and Parks**) and permeability (**Gallino, Boyce, Parks and Cohen**) properties. Here, we focus on the mechanical properties. **Rutledge and Manevitch** computed for the first time the elastic properties of a single lamella of montmorillonite consisting of two tetrahedral layers and the intervening octahedral layer. The elastic response of the atomically thin nanoplate was calculated from curves of force versus displacement obtained at slow rates

of deformation. Bending stiffness was estimated independently from the onset of nonlinear deformation under compression. The atomistic results were rationalized in terms of a continuum model for thin plates, but it was observed that on the nanometer length scale, the continuum concept of the elastic modulus becomes ambiguous, and must be replaced by such quantities as force borne per unit length. We obtained values of 250-260 N/m for Eh and 166 N/m for Gh , where E is the in-plane equivalent of Young's modulus, G is the in-plane equivalent of shear modulus, and h is the thickness of the nanoplate. The effective mechanical thickness of the clay lamella was found to be 0.78 nm, comparable to the distance between the outermost layers of atoms on either surface of the atomically thin sheet (0.615 nm). These values for the clay sheet properties together with the multiscale strategy have enabled our ability to predict the observed nanocomposite stiffness dependence on polymer type (whether the matrix is elastomer, glassy, or semicrystalline) and particle morphology (exfoliated, intercalated, degree of intercalation). Comparisons with mechanical data (**Sheng, Boyce, Parks**) obtained on MXD6 nylon/nanoclay samples provided by **Gilmer** (Eastman Chemical) and with the particle distribution and morphology characterized using TEM (**Cohen and Abes**) and WAXD (**McKinley and Lee**) showed excellent agreement with model predictions; the model was also found to predict a host of data on material systems in the literature (provided the morphological data was also provided on the literature samples).



Furthermore, the transcrystallization behavior of the matrix in semi-crystalline nanocomposites was also included in the numerical micromechanical models of **Sheng, Boyce and Parks** and have enabled careful study of the contribution of this special morphology on the end nanocomposite stiffness – which was found to be relatively small compared to the overall stiffening effect from the particles themselves.

As discussed above, the **Sheng, Boyce, Parks and Rutledge** multiscale modeling strategy accounts for the hierarchical morphology of the nanocomposite: at a lengthscale of thousands of microns, the structure is one of high aspect ratio particles within a matrix; at the lengthscale of microns, the clay particle structure is either (a) exfoliated clay sheets of nanometer level thickness or (b) stacks of parallel clay sheets separated from one

another by interlayer galleries of nanometer level height, and the matrix, if semi-crystalline, consists of fine lamella, oriented with respect to the polymer/nanoclay interfaces. Quantitative structural parameters are extracted from XRD patterns and TEM micrographs (the number of silicate sheets in a clay stack, N , and the silicate sheet layer spacing, $d_{(001)}$) are used to determine geometric features of the as-processed clay "particles", including L/t and the ratio of f_p to W_c . These geometric features, together with estimates of silica lamina elastic and thermal expansion properties obtained from molecular dynamics simulations, provide a basis for modeling effective thermal/mechanical properties of the clay particle. In the case of the semi-crystalline matrices (e.g., nylon 6), the transcrystallization behavior induced by the nanoclay is taken into account by modeling a layer of matrix surrounding the particle to be highly textured and therefore mechanically anisotropic. Micromechanical models (numerical as well as analytical) based on the "effective clay particle" were employed to calculate the overall anisotropic elastic constants. This approach was then further enhanced to also predict the anisotropic coefficient of thermal expansion (CTE) and anisotropic yield surface of the amorphous and semi-crystalline polymer-clay nanocomposites and to compute their dependence on the matrix and clay properties as well as internal clay structural parameters.

The proposed modeling technique captures the strong modulus enhancements observed in elastomer/clay nanocomposites as compared with the moderate enhancements observed in glassy and semi-crystalline polymer/clay nanocomposites. For the case where the matrix is semi-crystalline, the enhancements of composite modulus and strength are found to rely on different functions of the clay: while the modulus enhancement can be explained by the conventional role of "stiff filler", the strength enhancement of the nanocomposite mainly lies in the improvements of the matrix property achieved through the matrix transcrystallization induced by nanoclay the "nucleation sites". When the nanocomposite experiences a morphological transition from intercalated to completely exfoliated, an abrupt jump in the composite initial yield strength, as opposed to the moderate increase in the overall composite modulus, was predicted. The elastic moduli and anisotropic CTE for MXD6-clay and nylon 6-clay nanocomposites predicted by the micromechanical models are in excellent agreement with experimental data. In summary, continuum-based micromechanical models can provide robust predictions of the overall thermal/mechanical properties of polymer/clay nanocomposites, with the employment of a reliable method to account for the intrinsically hierarchical morphology of the nanoclay, and for the special matrix morphology and properties adjacent to the nanoclay.

These model predictions considered a strong interface between the matrix and the nanoclay which has been observed and confirmed in the FTIR studies of **Loo and Gleason**. For first time, stress-induced peak shifts in the Si-O stretching vibration of montmorillonite clay in a polymer nanocomposite system have been observed by FTIR. This methodology offers a way to monitor how the clay particles deform relative to the polymer matrix in order to achieve insights to micromechanics of nanoclay reinforced polymer matrices. The FTIR peaks corresponding to Si-O vibrations of montmorillonite clay in nylon 6 nanocomposite films were found to shift toward lower wavenumbers

upon the application of stress in the elastic regime. Small monotonic negative shifts of the montmorillonite clay FTIR peaks at 1018, 1046, and 1022 cm^{-1} was observed as strain was increase from an initial value of zero to a final value of 0.02. The 1018 cm^{-1} peak showed the greatest shift and the 1022 cm^{-1} the least shift. All three peaks revert to the frequency at zero strain upon brittle fracture, confirming that the observed shifts result from changes arising from the deformation of the clay platelets which can include alteration of the Si-O bond length and Si-O-Si angle. The observation of a stress induced frequency shift in the clay demonstrates that there is transfer of load from the bulk polymeric matrix to the nanoclay particles. These measurements were recently further quantified through a combination of molecular modeling by **Kalra** and **Rutledge** and micromechanical modeling by **Parks** to quantify the load transfer from the matrix to the particle and the relationship between the particle strain and the FTIR peak shifts.

The response of the polymeric matrix, nylon-6, was also studied. While pure nylon-6 is usually found in the α crystalline form, in the clay filled nanocomposites, both the α and γ crystalline regions are observed. The small strain deformation of α crystals in nylon 6 involves the weakening of hydrogen bonds between adjacent chains and broadening of the hydrogen bond strength distribution. At the same time, the tightly packed structure is opened up as the hydrogen bonds are weakened. The resulting crystal structure at higher stress has longer N-H---O and CH bonds. The fractional change in hydrogen bond length is much larger than that of the CH bond. The FTIR technique enables the changes in X-H bond length as small as 0.001% to be observed. This is the first time stress-induced frequency shifts of FTIR vibrations related to hydrogen bonds (NH stretch and amide II) have been observed. In the α crystals of nylon 6 the NH stretching mode shifts to higher frequencies and the amide II mode shifts toward lower frequencies with stress. This is consistent with the weakening of hydrogen bonds between chains and lengthening of the hydrogen bond distance during deformation. The effect of deformation on the weakening of hydrogen bonds in the γ crystals is more difficult to analyze, as the NH stretching mode does not shift much with stress. Among all the peaks studied, only the amide II mode showed substantial frequency shift. This could be the result of the alignment of the hydrogen bonds in the crystals at an angle to the stretching direction so that during deformation, the hydrogen bond length and angle changed in such a manner as to leave the NH stretch frequency fairly constant. The molecular changes of the α and γ crystals with deformation are consistent with computer simulations of their structures and serve as validation of the force fields used. The broadness and shape of the CH_2 stretching peaks in the α films also indicate the presence of at least two different CH_2 configurations.

4. Publications and Presentations

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Note that several additional papers from recent theses are still in preparation and will be forthcoming over the next year.

Theses:

S.M. Theses:

Sheng, Nuo, "Micro-Nanoscale Modeling of Anisotropic Mechanical Properties of Polymer/Layered-Silicate Nanocomposites", August 2002; supervisors: Boyce and Parks.

Grippe, C.P., "Design and Manufacture of a Deformation Stage for In-Situ Tensile Testing within an Atomic Force Microscope (AFM)", January, 2003; supervisors: Boyce and Bamberg.

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Parsons, Ethan, "Micromechanics of Polymers Containing Mineral Fillers", Mechanical Engineering, MIT, supervisors: Boyce and Parks, May, 2006.

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Aronow, Roger: "Toughenability of amorphous polymer / mineral filler composites", Chemical Engineering, May 2006, supervisor: Cohen

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Wang, B., "Rheological and Morphological Characterization of Hierarchically Nanostructured Materials", Chemical Engineering, May 2007, supervisors: McKinley and Cohen; partial support from DURINT.

Note that several additional papers from recent theses are still in preparation and will be forthcoming over the next year.

Presentations:

Mary C. Boyce, "Multiscale Modelling of Polymeric Nanocomposites", ExxonMobil, December 2001, Houston, TX.

Mary C. Boyce, "Multiscale Modelling of Mechanical and Transport Behavior of Polymeric Nanocomposites", April, 2002, MRS Meeting, San Francisco.

Mary C. Boyce, "Micro/Nanomechanical Modelling of Polymeric Nanocomposites", April, 2002, ACS Meeting, Orlando.

Mary C. Boyce, "Micro and Macromechanics of Filled Polymers", July, 2002, EUROMECH, Vienna.

Hojun Lee and Gareth McKinley, "Rheological Properties, Processing and Morphology of Polymer- Layered Silicate Nanocomposites", Society of Rheology, Minneapolis, October, 2002.

Mary C. Boyce, "Mechanics of the Indentation of Vertically Aligned Carbon Nanotube Coatings", Symposium in honor of 60th Birthday of L.B. Freund, California Institute of Technology, January 2003.

A. Pantano, D.M. Parks and M.C. Boyce, "Mechanics of Deformation of Single and Multiwall Carbon Nanotubes", American Physical Society, March Meeting, 2003, Austin, TX.

Hang (Jerry) Qi, "Effects of Dimensions and Processing Conditions on the Mechanical Properties of Carbon Nanotubes and Vertically Aligned Carbon Nanotube Forests", APS Meeting, Austin, TX, March 2003.

Nuo Sheng, "Multiscale Micromechanical Modeling of Polymer/Clay Nanocomposites and the Effective Clay Particle", APS Meeting, Austin, TX, March 2003.

Mary C. Boyce, "Mechanics of Carbon Nanotubes and Vertically Aligned Carbon Nanotube Arrays", University of Illinois – Urbana, April 2003.

Hang (Jerry) Qi, "On Determining the Mechanical Properties of Carbon Nanotubes and Vertically Aligned Carbon Nanotube Forests Using Nanoindentation", MRS Spring Meeting, San Francisco, CA, April 21-25, 2003.

A. Pantano, D.M. Parks and M.C. Boyce, "Mechanics of Deformation of Single and Multiwall Carbon Nanotubes", Horizon Nanoevent Meeting, Cambridge, U.K., April 9, 2003.

A. Pantano, D.M. Parks and M.C. Boyce, "Mechanics of Deformation of Single and Multiwall Carbon Nanotubes", 2003 Materials Research Society Spring Meeting, San Francisco, CA, April 21-25, 2003.

A. Pantano, D.M. Parks and M.C. Boyce, "A Finite-Element Technology for Modeling Single and Multiwall Carbon Nanotubes", Second M.I.T. Conference on Computational Fluid and Solid Mechanics, Cambridge, MA, June 17-20, 2003.

E.T. Kopesky, G.H. McKinley, R.E. Cohen, T.S. Haddad, "Morphological Effects of Tethered and Untethered Polyhedral Oligosilsesquioxanes (POSS) on the Viscometric and Linear Viscoelastic Properties of PMMA", Symposium on Liquid Crystalline Polymers, Self-Assembling Fluids and Nanomaterials, 75th Annual Meeting of the Society of Rheology, Pittsburgh, PA, October 12-17, 2003.

A. Pantano, M. C. Boyce and D. M. Parks, "Nonlinear Structural Mechanics Based Modeling of Carbon Nanotube Deformation", 40th Annual Technical Meeting Society of Engineering Science, Ann Arbor, Michigan, October 12-15, 2003.

Theodora Tzianetopoulou, "Micromechanics of PS/PB/PS Triblock-Copolymer Films with Lamellar Morphology", MRS Meeting, Dec 1-5, 2003, Boston, MA.

Nuo Sheng, "Micromechanical Modeling of Polymer/Clay Nanocomposites", MRS Meeting, Dec 1-5, 2003, Boston, MA.

Michelle Poliskie, "Static Uniaxial Compression of Polyisoprene-Montmorillonite Nanocomposites Monitored by ¹H Spin-Lattice Relaxation Time Constants", MRS Meeting, Dec 1-5, 2003, Boston, MA.

Kenneth Lau, "Chemical Vapor Surface Modification of Carbon Nanotubes and Its Effect on the Mechanical Properties of Nanocomposites with Poly(Methyl Methacrylate)" MRS Meeting, Dec 1-5, 2003, Boston, MA.

Antonio Pantano, "Nonlinear Structural Mechanics Based Modeling of Carbon Nanotube Deformation", MRS Meeting, Dec 1-5, 2003, Boston, MA.

Hang (Jerry) Qi, "Nanoindentation and Nanoscratch of Vertically Aligned Carbon Nanotubes, PTFE and PMMA Coated Carbon Nanotubes, and ZnO Nanofibers", MRS Meeting, Dec 1-5, 2003, Boston, MA.

T Tzianetopoulou and MC Boyce. Micromechanics of PS/PB/PS triblock-copolymer films with lamellar morphology, Fall MRS Meeting Boston, December 2003.

F.M. Capaldi, M.C. Boyce, G.C. Rutledge "Atomistic Simulations of Elastic-Plastic Deformation of an Amorphous Polymer", Proc. Am. Chem.Soc. Div. Polym. Mater.: Sci. and Eng. **2001**, 85 (Chicago, IL), 552-553.

A. Kalra and G.C. Rutledge, "Vibrational Spectrum From Molecular Simulations: Polymers And Clay", PMSE Preprints, 2004, 91, 902-903 (American Chemical Society, Philadelphia, PA, Aug. 22-26, **2004**).

Rutledge et al, "*Molecular Level Modeling of Nanocomposites*", Wright Patterson Air Force Base, Dayton, OH June 17, **2004**.

Boyce, M.C., "Mechanics of Polymer Nanocomposites", WPAFB, Dayton, OH, March 15, 2004.

Boyce, M.C., "Mechanics of NanoIndentation and Nanoscratch of Vertically Aligned Carbon Nanotubes", CMI Group Meeting with Industry, Moller Center, Churchill College, Cambridge, UK, June 25, 2004.

Boyce, M.C., "Mechanics of Carbon Nanotubes and Carbon Nanotube/Polymer Nanocomposites", MRS Fall 2004 Invited Lecture, Boston, MA, December 2004.

Boyce, M.C., "Mechanics of Polymer Nanocomposites", ACS PMSE Invited Lecture, Spring 2005, March 2005, San Diego, CA.

F.M Capaldi, M.C. Boyce, G.C. Rutledge, "Modeling the interface between POSS and polymer", PMSE Preprints, 93, 920, 2005 (American Chemical Society, Washington DC, Aug 28-Sept 1, **2005**).

Rutledge et al, "Molecular Simulation of Structure and Dynamics in Nanocomposites", 5th International Discussion Meeting on Relaxations in Complex Systems (SIDMRCS), Lille, France, July 7-13, **2005**. Also at ACS Symposium on Complex Fluids in Confined Spaces, Atlanta, GA, Mar 26-30, **2006**)

Boyce, M.C., "Mechanics of Polymer Nanocomposites", ExxonMobil, Baytown, TX, June, 2005.

Boyce, M.C., "Mechanics of Filled Polymers", Cabot Corporation, Billerica, MA February 2006.

Boyce, M.C., "Mechanics of Carbon Nanotube Elastomer Nanocomposites", ACS Rubber Division Plenary Lecture, Akron, OH , May, 2006.

Parks, D. M. "Structure, Stiffness, and Strength: Continuum Mechanics Modeling of Clay-Reinforced Polymer Nanocomposites", Dipartimento di Meccanica di Palermo July 10, 2006 .

Parks, D. M. "Structure, Stiffness, and Strength: Continuum Mechanics Modeling of Clay-Reinforced Polymer Nanocomposites", University of Texas at Austin, April 12, 2007 .

Parks, D. M. "Structure, Stiffness, and Strength: Continuum Mechanics Modeling of Clay-Reinforced Polymer Nanocomposites", Ecole des Mines de Paris, April 26, 2007 .